

## CLAIMS

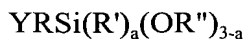
What is claimed is:

1. A method for increasing the hardness of silica/rubber mixtures comprising blending with said mixture at least one silane and a hardness-increasing amount of at least one member selected from the group consisting of thixotropic fumed silica; precipitated silica; an MQ resin wherein Q is  $\text{SiO}_{4/2}$ , M is  $\text{R}^1\text{R}^2\text{R}^3\text{SiO}_{1/2}$ , and  $\text{R}^1$ ,  $\text{R}^2$ , and  $\text{R}^3$  are the same or different functional or non-functional organic groups; carbon black; a thermoplastic resin; and a thermosetting resin.

2. The method of claim 1 wherein the silane is an organofunctional silane comprising at least one alkoxy group per silicon atom.

3. The method of claim 2 wherein the organofunctional moiety of the organofunctional silane is selected from the group consisting of mercapto, sulfide, disulfide, polysulfide, vinyl, acetylene, ureido, carboxyl, carbonyl, amino, epoxy, and halide.

4. The method of claim 2 wherein the organofunctional silane is defined by the formula:



wherein

R is a divalent alkylene, arylene, or aralkylene group of 1 to 20 carbon atoms, a vinyl group, or acetylenyl;

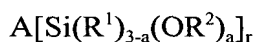
R' is a monovalent alkyl, aryl, or aralkyl group of 1 to 10 carbon atoms;

R'' is a monovalent alkyl, aryl, or aralkyl group of 1 to 12 carbon atoms, wherein one or more of the carbon atoms can be replaced with a heteroatom;

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Y is an organofunctional group selected from the group consisting of mercapto, sulfides, and polysulfides of the structure  $R'''-S_x-$  where  $R'''$  is a monovalent alkyl, aryl, or aralkyl group of 1 to 20 carbon atoms or the radical  $-RSiR'_a(OR'')_{3-a}$ , and x is 1 to 9, which resulting molecule must contain at least one alkoxysilane bond; other bis, tris, and higher silanes with sulfur or other heteroatom linkages in the groups between the alkoxy silane groups; vinyl; acetylenyl; carbonyl; amino; alkyl, aralkyl, or aryl substituted amino; ureido; thiocyanate; thiourea; epoxy; and hydrogen; and a is an integer and is 0, 1, or 2.

5. The method of claim 2 wherein the organofunctional silane is defined by the formula:



wherein

A is a group of valence r, r being an integer greater than or equal to 1, selected from the group consisting of linear, branched, or cyclic hydrocarbon groups, an oxygen atom, or a linear, branched, or cyclic siloxane or polysiloxane group, each of which, save an oxygen atom, may contain substituents with oxygen, nitrogen, sulfur, or halogen heteroatoms;

$R^1$  is selected from the group consisting of hydrocarbyl, hydrogen, and chain-substituted hydrocarbyl;

$R^2$  is selected from the group consisting of hydrocarbyl and chain-substituted hydrocarbyl; and

a is 0, 1, 2, or 3.

6. The method of claim 1 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.

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7. The method of claim 1 wherein the silica/rubber mixture further comprises an inorganic filler.

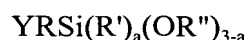
8. The method of claim 7 wherein the inorganic filler is selected from the group consisting of titanium dioxide, aluminosilicate, alumina, calcium carbonate, carbon fibers, glass fibers, kaolin clay, mica, talc, wollastonite alumina, calcium carbonate, carbon fibers, glass fibers, kaolin clay, mica, talc, wollastonite

9. The method of claim 1 wherein the member is thixotropic- (hydrophilic and hydrophobic) fumed (pyrogenic) silica.

10. The method of claim 9 wherein the silane is an organofunctional silane comprising at least one alkoxy group per silicon atom.

11. The method of claim 10 wherein the organofunctional moiety of the organofunctional silane is selected from the group consisting of mercapto, sulfide, disulfide, polysulfide, vinyl, acetylene, ureido, carboxyl, carbonyl, amino, epoxy, and halide.

12. The method of claim 10 wherein the organofunctional silane is defined by the formula:



wherein

R is a divalent alkylene, arylene, or aralkylene group of 1 to 20 carbon atoms, a vinyl group, or acetylenyl;

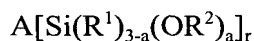
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R' is a monovalent alkyl, aryl, or aralkyl group of 1 to 10 carbon atoms;

R'' is a monovalent alkyl, aryl, or aralkyl group of 1 to 12 carbon atoms, wherein one or more of the carbon atoms can be replaced with a heteroatom;

Y is an organofunctional group selected from the group consisting of mercapto, sulfides, and polysulfides of the structure R'''-S<sub>x</sub>- where R''' is a monovalent alkyl, aryl, or aralkyl group of 1 to 20 carbon atoms or the radical -RSiR'<sub>a</sub> (OR'')<sub>3-a</sub>, and x is 1 to 9, which resulting molecule must contain at least one alkoxy silane bond; other bis, tris, and higher silanes with sulfur or other heteroatom linkages in the groups between the alkoxy silane groups; vinyl; acetylenyl; carbonyl; amino; alkyl, aralkyl, or aryl substituted amino; ureido; thiocyanate; thiourea; epoxy; and hydrogen; and a is an integer and is 0, 1, or 2.

13. The method of claim 10 wherein the organofunctional silane is defined by the formula:



wherein

A is a group of valence r, r being an integer greater than or equal to 1, selected from the group consisting of linear, branched, or cyclic hydrocarbon groups, an oxygen atom, or a linear, branched, or cyclic siloxane or polysiloxane group, each of which, save an oxygen atom, may contain substituents with oxygen, nitrogen, sulfur, or halogen heteroatoms;

R<sup>1</sup> is selected from the group consisting of hydrocarbyl, hydrogen, and chain-substituted hydrocarbyl;

R<sup>2</sup> is selected from the group consisting of hydrocarbyl and chain-substituted hydrocarbyl; and

a is 0, 1, 2, or 3.

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1        14.        The method of claim 9 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.

1        15.        The method of claim 9 wherein the silica/rubber mixture further comprises an  
2 inorganic filler.

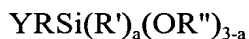
1        16.        The method of claim 15 wherein the inorganic filler is selected from the group  
2 consisting of titanium dioxide, aluminosilicate, alumina, calcium carbonate, carbon fibers,  
3 glass fibers, kaolin clay, mica, talc, wollastonite alumina, calcium carbonate, carbon fibers,  
4 glass fibers, kaolin clay, mica, talc, wollastonite

1        17.        The method of claim 1 wherein the member is precipitated silica.

1        18.        The method of claim 17 wherein the silane is an organofunctional silane comprising  
2 at least one alkoxy group per silicon atom.

1        19.        The method of claim 18 wherein the organofunctional moiety of the organofunctional  
2 silane is selected from the group consisting of mercapto, sulfide, disulfide, polysulfide, vinyl,  
3 acetylene, ureido, carboxyl, carbonyl, amino, epoxy, and halide.

1        20.        The method of claim 18 wherein the organofunctional silane is defined by the  
2 formula:



4        wherein

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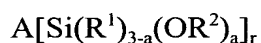
1 R is a divalent alkylene, arylene, or aralkylene group of 1 to 20 carbon atoms, a vinyl  
2 group, or acetylenyl;

3 R' is a monovalent alkyl, aryl, or aralkyl group of 1 to 10 carbon atoms;

4 R" is a monovalent alkyl, aryl, or aralkyl group of 1 to 12 carbon atoms, wherein one  
5 or more of the carbon atoms can be replaced with a heteroatom;

6 Y is an organofunctional group selected from the group consisting of mercapto,  
7 sulfides, and polysulfides of the structure R'''-S<sub>x</sub>- where R''' is a monovalent alkyl, aryl, or  
8 aralkyl group of 1 to 20 carbon atoms or the radical -RSiR'<sub>a</sub>(OR'')<sub>3-a</sub>, and x is 1 to 9, which  
9 resulting molecule must contain at least one alkoxysilane bond; other bis, tris, and higher  
10 silanes with sulfur or other heteroatom linkages in the groups between the alkoxy silane  
11 groups; vinyl; acetylenyl; carbonyl; amino; alkyl, aralkyl, or aryl substituted amino; ureido;  
12 thiocyanate; thiourea; epoxy; and hydrogen; and a is an integer and is 0, 1, or 2.

1 21. The method of claim 18 wherein the organofunctional silane is defined by the  
2 formula:



4 wherein

5 A is a group of valence r, r being an integer greater than or equal to 1, selected from  
6 the group consisting of linear, branched, or cyclic hydrocarbon groups, an oxygen atom, or a  
7 linear, branched, or cyclic siloxane or polysiloxane group, each of which, save an oxygen  
8 atom, may contain substituents with oxygen, nitrogen, sulfur, or halogen heteroatoms;

9 R<sup>1</sup> is selected from the group consisting of hydrocarbyl, hydrogen, and chain-  
10 substituted hydrocarbyl;

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11           R<sup>2</sup> is selected from the group consisting of hydrocarbyl and chain-substituted  
12 hydrocarbyl; and  
13           a is 0, 1, 2, or 3.

1       22.    The method of claim 17 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.

1       23.    The method of claim 17 wherein the silica/rubber mixture further comprises an  
2 inorganic filler.

1       24.    The method of claim 23 wherein the inorganic filler is selected from the group  
2 consisting of titanium dioxide, aluminosilicate, alumina, calcium carbonate, carbon fibers,  
3 glass fibers, kaolin clay, mica, talc, wollastonite alumina, calcium carbonate, carbon fibers,  
4 glass fibers, kaolin clay, mica, talc, wollastonite

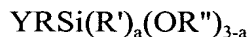
1       25.    The method of claim 1 wherein the member is an MQ resin.

1       26.    The method of claim 25 wherein the silane is an organofunctional silane comprising  
2 at least one alkoxy group per silicon atom.

1       27.    The method of claim 26 wherein the organofunctional moiety of the organofunctional  
2 silane is selected from the group consisting of mercapto, sulfide, disulfide, polysulfide, vinyl,  
3 acetylene, ureido, carboxyl, carbonyl, amino, epoxy, and halide.

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28. The method of claim 26 wherein the organofunctional silane is defined by the formula:



wherein

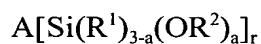
R is a divalent alkylene, arylene, or aralkylene group of 1 to 20 carbon atoms, a vinyl group, or acetylenyl;

R' is a monovalent alkyl, aryl, or aralkyl group of 1 to 10 carbon atoms;

R'' is a monovalent alkyl, aryl, or aralkyl group of 1 to 12 carbon atoms, wherein one or more of the carbon atoms can be replaced with a heteroatom;

Y is an organofunctional group selected from the group consisting of mercapto, sulfides, and polysulfides of the structure  $\text{R}'''-\text{S}_x-$  where  $\text{R}'''$  is a monovalent alkyl, aryl, or aralkyl group of 1 to 20 carbon atoms or the radical  $-\text{RSiR}'_a(\text{OR}'')_{3-a}$ , and x is 1 to 9, which resulting molecule must contain at least one alkoxysilane bond; other bis, tris, and higher silanes with sulfur or other heteroatom linkages in the groups between the alkoxy silane groups; vinyl; acetylenyl; carbonyl; amino; alkyl, aralkyl, or aryl substituted amino; ureido; thiocyanate; thiourea; epoxy; and hydrogen; and a is an integer and is 0, 1, or 2.

29. The method of claim 26 wherein the organofunctional silane is defined by the formula:



wherein

A is a group of valence r, r being an integer greater than or equal to 1, selected from the group consisting of linear, branched, or cyclic hydrocarbon groups, an oxygen atom, or a



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linear, branched, or cyclic siloxane or polysiloxane group, each of which, save an oxygen atom, may contain substituents with oxygen, nitrogen, sulfur, or halogen heteroatoms;

$R^1$  is selected from the group consisting of hydrocarbyl, hydrogen, and chain-substituted hydrocarbyl;

$R^2$  is selected from the group consisting of hydrocarbyl and chain-substituted hydrocarbyl; and

a is 0, 1, 2, or 3.

30. The method of claim 25 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.

31. The method of claim 25 wherein the silica/rubber mixture further comprises an inorganic filler.

32. The method of claim 31 wherein the inorganic filler is selected from the group consisting of titanium dioxide, aluminosilicate, alumina, calcium carbonate, carbon fibers, glass fibers, kaolin clay, mica, talc, wollastonite alumina, calcium carbonate, carbon fibers, glass fibers, kaolin clay, mica, talc, wollastonite

33. The method of claim 1 wherein the member is carbon black.

34. The method of claim 33 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.

35. The method of claim 1 wherein the member is a thermoplastic resin.

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- 1     36.     The method of claim 35 wherein the thermoplastic resin is selected from the group  
2     consisting of high-density polyethylene, ultra high molecular weight polyethylene, and low  
3     density-polyethylene.
- 1     37.     The method of claim 35 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.
- 1     38.     The method of claim 1 wherein the member is a thermosetting resin.
- 1     39.     The method of claim 1 wherein the resin is a high glass transition resin.
- 1     40.     The method of claim 39 wherein the high glass transition resin is selected from the  
2     group consisting of polyphenylene sulfide, polyamide, polyimide, polyamide-imide,  
3     polycarbonate, nylons, and polymethylmethacrylate.
- 1     41.     The method of claim 39 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.
- 1     42.     An article of manufacture comprising a silica/rubber mixture hardened by blending  
2     with said mixture at least one silane and a hardness-increasing amount of at least one member  
3     selected from the group consisting of thixotropic fumed silica; precipitated silica; an MQ  
4     resin wherein Q is  $\text{SiO}_{4/2}$ , M is  $\text{R}^1\text{R}^2\text{R}^3\text{SiO}_{1/2}$ , and  $\text{R}^1$ ,  $\text{R}^2$ , and  $\text{R}^3$  are the same or different  
5     functional or non-functional organic groups; carbon black; a thermoplastic resin; and a  
6     thermosetting resin.
- 1     43.     The article of claim 42 wherein the silane is 3-octanoylthio-1-propyltriethoxysilane.

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1      44.      The article of claim 42 wherein said article is a tire.

1      45.      The article of claim 43 wherein said article is a tire.